

FTIR STUDY OF COMPETITIVE WATER-ARENE SORPTION ON TETRAMETHYLAMMONIUM- AND TRIMETHYLPHENYLAMMONIUM-MONTMORILLONITES

JEFFREY J. STEVENS, SHARON J. ANDERSON, AND STEPHEN A. BOYD

Department of Crop and Soil Sciences, Michigan State University,
East Lansing, Michigan 48824

Abstract—Montmorillonites saturated with small quaternary alkylammonium ions such as tetramethylammonium (TMA) or trimethylphenylammonium (TMPA) are excellent sorbents for aromatic pollutants. In some cases, water inhibits arene sorption, but the inhibition mechanism is not understood completely. The objectives of this study were to determine whether arenes interact with adsorbed TMA and TMPA ions and/or with siloxane surfaces, and how water affects these interactions. We reacted benzene and ethylbenzene vapors with normal- and reduced-charge TMA- and TMPA-montmorillonite films at several relative humidities, and obtained infrared spectra of the resulting sorbate-clay complexes. Arene sorption caused the methyl asymmetric deformation vibrations adsorbed TMA and TMPA to shift to lower wavenumber, whereas water sorption caused shifts to higher wavenumber. In the absence of water, benzene and ethylbenzene adsorbed on the siloxane surface as well as interacted directly with TMA and TMPA ions. The proportion of TMA and TMPA ions that interacted with benzene and ethylbenzene was greater for reduced-charge than normal-charge montmorillonite. Comparison of the HOH deformation and cation methyl asymmetric deformation vibrations indicated that both benzene and ethylbenzene inhibited water sorption substantially, and that water more readily displaced benzene and ethylbenzene from TMA and TMPA ions than from siloxane surfaces. Water inhibited arene sorption mainly by hydrating exchangeable cations, thereby obscuring siloxane surfaces adjacent to adsorbed TMA and TMPA ions and decreasing the average pore dimensions. These results indicate that in the presence of bulk water, arene adsorption likely occurs primarily on the siloxane surface.

Key Words—Alkylammonium, Benzene, Ethylbenzene, Infrared spectroscopy, Organoclay, Sorption, Water.

INTRODUCTION

Clays saturated with quaternary alkylammonium cations have been proposed as sorbents to remove organic pollutants from aqueous industrial waste streams (Boyd et al. 1991). Aromatic pollutant sorption on clays saturated with small alkylammonium ions such as tetramethylammonium (TMA) and trimethylphenylammonium (TMPA) is affected by clay charge density, the presence of water, and arene size. Charge-density effects were first noted by Lee et al. (1990) and Jaynes and Boyd (1990), who found that low-charge TMA- and TMPA-montmorillonite generally sorbed larger quantities of arenes than did high-charge TMA- and TMPA-montmorillonite, for both vapor-phase and aqueous-phase sorption. A similar increase in aqueous-phase arene sorption with decreasing surface-charge density, and hence with an increasing area of uncharged siloxane surface for a range of TMPA-montmorillonites led Jaynes and Boyd (1991) to conclude that arenes adsorb preferentially onto uncharged siloxane surfaces. They further concluded that adsorbed TMPA ions are not involved directly in aqueous-phase arene sorption, but prop open the clay layers so that arenes can penetrate the interlamellar region and adsorb on uncharged siloxane surfaces.

Sorption of alkylbenzenes on TMA-montmorillonite

decreases with increasing number or size of alkyl substituents on the benzene ring. In addition, water inhibits sorption of larger methylbenzenes, such as xylene, more than sorption of toluene or benzene (Lee et al. 1990). Jaynes and Boyd (1991) found that aqueous-phase alkylbenzene sorption on TMPA-montmorillonite decreased as the length of the alkyl substituent increased, though the decrease was only substantial for a high-charge, tetrahedrally substituted smectite. These studies have shown that water inhibits arene sorption, yet the exact cause of this inhibition is not understood fully. Infrared studies of water sorption on TMA- and TMPA-montmorillonites have shown that water preferentially hydrates TMA and TMPA cations, not the siloxane surface, at low partial pressures of water (Stevens and Anderson 1996b). Water in the hydration shells of TMA and TMPA may prevent arene-cation interactions and also may reduce arene sorption on the siloxane surface by covering parts of the siloxane surface that would be accessible to arenes on dry clay, and by reducing the dimensions of interlamellar pores (between cations) through which arenes can diffuse. On low-charge clay, hydrated cations are farther apart, leaving more space in which arenes can diffuse and sorb.

This paper describes infrared spectroscopic investigations to determine the mechanism by which water

Table 1. Properties of normal- and reduced-charge TMA- and TMPA-montmorillonites.

Clay type	$d_{(001)}$	N_2 surface area ¹	Total C ²	Adsorbed cation ³
Å	$m^2 kg^{-1}$	$g kg^{-1}$	$mmol kg^{-1}$	
Reduced TMA	13.6 ± 0.3	289 ± 30	27.7 ± 0.7	474 ± 14
Normal TMA	13.6 ± 0.2	202 ± 26	40.7 ± 0.3	847 ± 6
Reduced TMPA	13.9 ± 0.6	318 ± 14	48.6 ± 0.9	449 ± 8
Normal TMPA	14.9 ± 0.3	252 ± 28	88.1 ± 1.0	814 ± 11

¹ Avg \pm SD (N = 2 or 3) from three-point BET N_2 adsorption isotherms using a Quantachrome Quantasorb Jr. surface area analyzer.

² Avg \pm SD (N = 2) of total C determined by combustion at 900°C using a Dohrmann DC-190 high-temperature carbon analyzer.

³ Avg \pm SD (N = 2) calculated with the equation: Adsorbed cation Total g C/kg clay \times mmol cation/g C.

inhibits arene sorption on TMA- and TMPA-montmorillonites. The first objective was to determine whether benzene and ethylbenzene interact with adsorbed TMA and TMPA ions, with the siloxane surface, or both, in the presence and absence of adsorbed water. The second objective was to determine whether arene-cation interactions increase or decrease as a clay's surface-charge density increases. A third objective was to learn whether arene size affects cation-arene interactions in the presence and absence of water, or if the previously reported decrease in arene sorption with increasing arene size is due solely to decreased accessibility of siloxane surfaces. Our final objective was to determine whether water sorption causes a decrease in arene sorption, or vice versa, on the siloxane surface itself.

MATERIALS AND METHODS

Preparation of Organoclay Films

Wyoming montmorillonite (SWy-1) was obtained from the Clay Minerals Society Source Clays Repository at the University of Missouri-Columbia. The <2- μ m fraction was separated from coarser material by sedimentation and was saturated with either LiCl or NaCl as described previously (Stevens and Anderson 1996a). Reduced-charge clay was prepared using a method similar to that described by Brindley and Ertem (1971). A 50:50 mixture of Li-montmorillonite and Na-montmorillonite was freeze-dried, then heated to 250°C to promote Li migration into vacant octahedral sites. Reduced-charge clay was then re-expanded by sonicating 2-g subsamples in 200 ml of a 70% methanol-water mixture for 20 min in an ice-water bath (Greene-Kelly 1953; Brindley and Ertem 1971; Jaynes and Bigham 1987).

To prepare TMA- and TMPA-montmorillonites, TMA chloride and TMPA bromide were added to normal-charge and reduced-charge clays in 70% methanol-water suspensions and stirred for 72 h. Either TMA chloride or TMPA bromide were added to the clays in excess of the CEC. The clays then were dialyzed until halide-free and were freeze-dried. Physical

properties of the normal- and reduced-charge TMA- and TMPA-montmorillonites are listed in Table 1.

Seventy mg each of normal- and reduced-charge TMA- and TMPA-montmorillonite were suspended in 10 ml of methanol by sonicating for three 10-min intervals in an ice bath. After the third sonication, coarse material was allowed to settle from suspension, and 1-ml aliquots of the remaining clay suspension were pipetted onto 13-mm diameter Delrin[®] AgCl Disks (E.I. duPont de Nemours[®]) and air-dried. The pipetting was repeated several times to obtain a sufficiently thick film, defined as a film for which the clay O-H stretching vibration at 3650 cm^{-1} was approximately 20% transmittance. The amount of clay on the disks was $0.8 \pm 0.15 mg cm^{-2}$.

Competitive Water and Arene Vapor Sorption on Clay Films

Normal-charge and reduced-charge TMA- and TMPA-montmorillonite films were equilibrated overnight in a desiccator that contained a liquid reservoir of benzene, benzene- d_6 , or ethylbenzene, and either P_2O_5 or an aqueous salt solution to control the partial pressure of water vapor (Weast 1986). The reservoir of organic liquid provided an atmosphere that was saturated with respect to that arene. Both benzene and benzene- d_6 were used with TMA-montmorillonite because preliminary experiments showed that the ν_{19} ring stretching vibration of benzene overlapped with the methyl asymmetric deformation vibration of adsorbed TMA, while the C-D out-of-plane vibration of benzene- d_6 was out of the mid-infrared spectral region (Varsányi 1969). After overnight equilibration in the desiccator, each film was transferred rapidly into a gas-tight infrared cell (Stevens and Anderson 1996b) and re-equilibrated for 75 min. at the same partial water pressure as in the desiccator. The cell did not contain an arene reservoir because arene vapor peaks made it impossible to accurately determine the wavenumber position of infrared bands for sorbed arenes. Spectra of each of the four clay films were obtained first with no arene or water sorbed (i.e., dried over P_2O_5), then

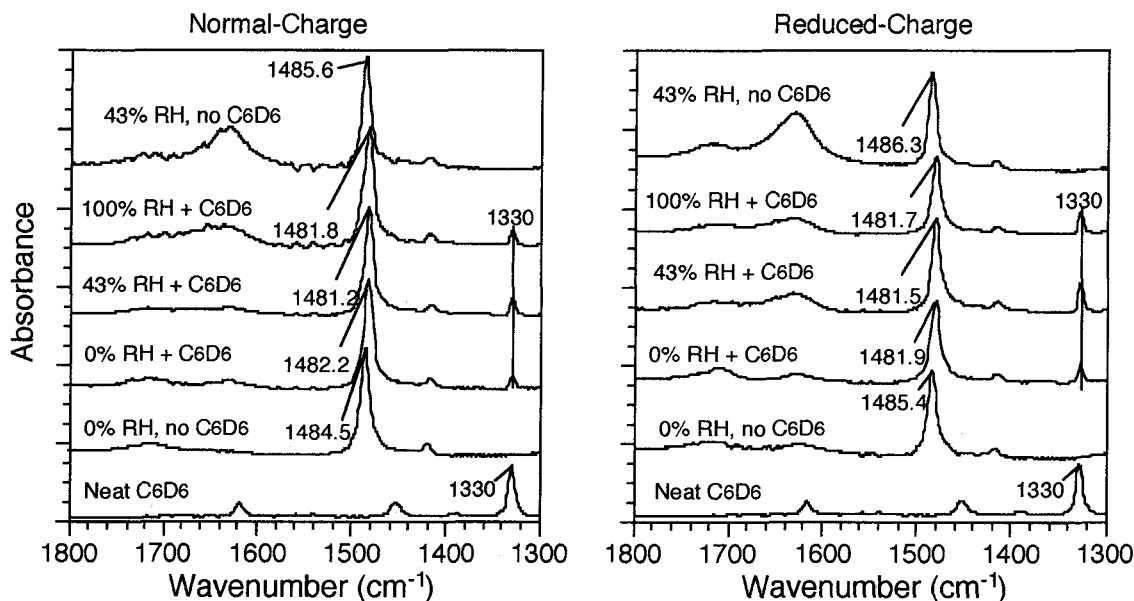


Figure 1. Infrared spectra of A) normal-charge and B) reduced-charge TMA-montmorillonites with and without sorbed benzene- d_6 (0 to 100% RH) and water (0 and 43% RH). Peak positions were estimated from peak center-of-mass. Spectrum of neat benzene- d_6 is shown at bottom.

with arene sorbed over P_2O_5 , then with arene sorbed at increasing partial pressure of water.

Single-beam infrared spectra of clay films with sorbed benzene and ethylbenzene were collected using a Perkin-Elmer 1600 FTIR spectrophotometer with a DTGS detector, 2 cm^{-1} resolution, no apodisation and 50 to 75 scans. The sample compartment and detector were purged with dry, CO_2 -free air that was obtained by passing compressed air through Drierite®, molecular sieve 4A, and ascarite®. Single-beam spectra of clay films with sorbed benzene- d_6 were collected using an N_2 -purged Nicolet IR/42 FTIR with a DTGS detector, 2 cm^{-1} resolution, Happ-Genzel apodisation and 100 scans. Single-beam background spectra were collected with a clean AgCl disk in the sample holder over the appropriate salt or acid solution in the IR cell. All spectra were stored on diskette and imported into the MS-DOS program SpectraCalc® (Galactic Software Inc.), then transformed into absorbance units. Spectra were smoothed using an 11-point Savitsky-Golay procedure. The baseline was leveled along six or seven baseline points in the spectrum, then zeroed. When there was no peak overlap, peak locations were determined by calculating the center of mass, using the wavenumber as the position vector and the incremental intensities of the peak as the mass vector. When peak overlap prevented use of the center-of-mass method, the position of the peak maximum was calculated. Differences of less than 2 cm^{-1} between peak maxima were not considered significant unless smaller changes were part of a general, consistent trend of increasing or decreasing wavenumber.

RESULTS

Methyl Deformation Vibrations of TMA and TMPA

ARENE SORPTION ON DRY MONTMORILLONITE. Infrared spectra of dry, normal- and reduced-charge TMA- and TMPA-montmorillonites with and without sorbed arenes (0% RH spectra in Figures 1 through 4) provide information about possible interactions between arenes and adsorbed TMA and TMPA ions. Benzene- d_6 sorption caused the methyl asymmetric deformation vibration (δ_a ; 1485 cm^{-1}) of TMA to shift 3 cm^{-1} to lower wavenumber on both normal-charge and reduced-charge TMA-montmorillonite (Figures 1A and 1B). Ethylbenzene sorption in the absence of water caused TMA's methyl δ_a vibration to shift 1 cm^{-1} to lower wavenumber on normal-charge montmorillonite and 2 cm^{-1} to lower wavenumber on reduced-charge montmorillonite (0% RH spectra in Figures 2A and 2B). These shifts are slightly smaller than those caused by benzene- d_6 sorption.

On normal-charge TMPA-montmorillonite, benzene sorption at 0% RH caused the methyl δ_a vibration of TMPA (1488 cm^{-1}) to shift 1 cm^{-1} to lower wavenumber (Figure 3A). On reduced-charge TMPA-montmorillonite, benzene sorption caused the δ_a peak (1490 cm^{-1}) to shift 4 cm^{-1} to lower wavenumber (Figure 3B). Ethylbenzene sorption at 0% RH caused TMPA's methyl δ_a vibration to shift 1 cm^{-1} to lower wavenumber on normal-charge montmorillonite and 3 cm^{-1} to lower wavenumber on reduced-charge montmorillonite (Figures 4A and 4B).

WATER-ARENE COMPETITION. When water alone was adsorbed on both normal- and reduced-charge TMA-

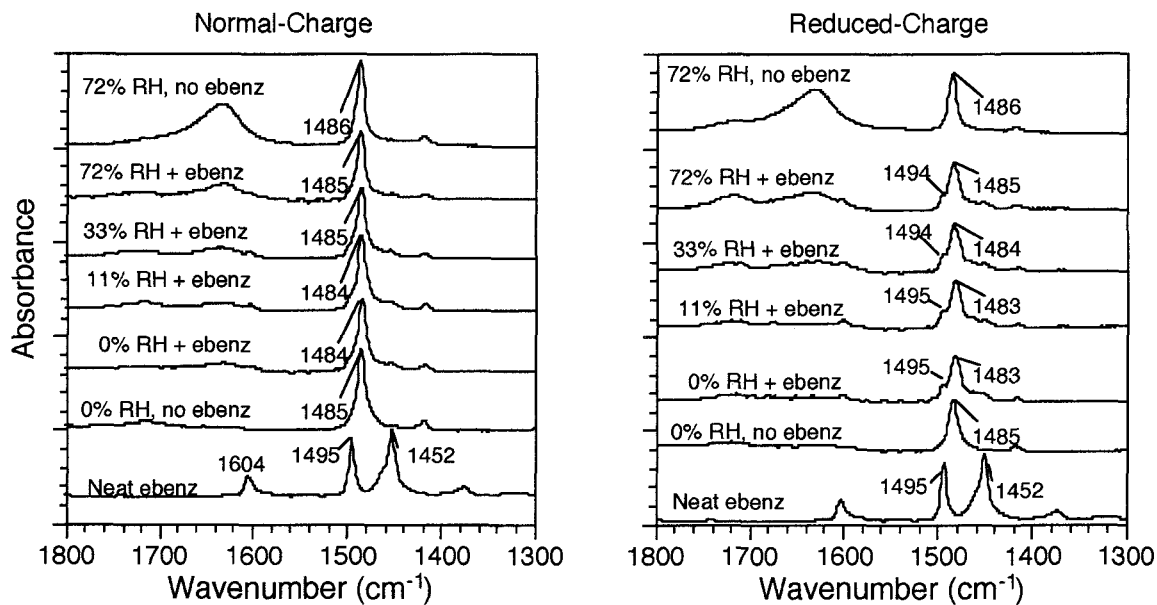


Figure 2. Infrared spectra of A) normal-charge and B) reduced-charge TMA-montmorillonites with and without sorbed ethylbenzene (0 to 72% RH) and water (0 and 72% RH). Peak positions were estimated from peak maxima. Spectrum of neat ethylbenzene is shown at bottom.

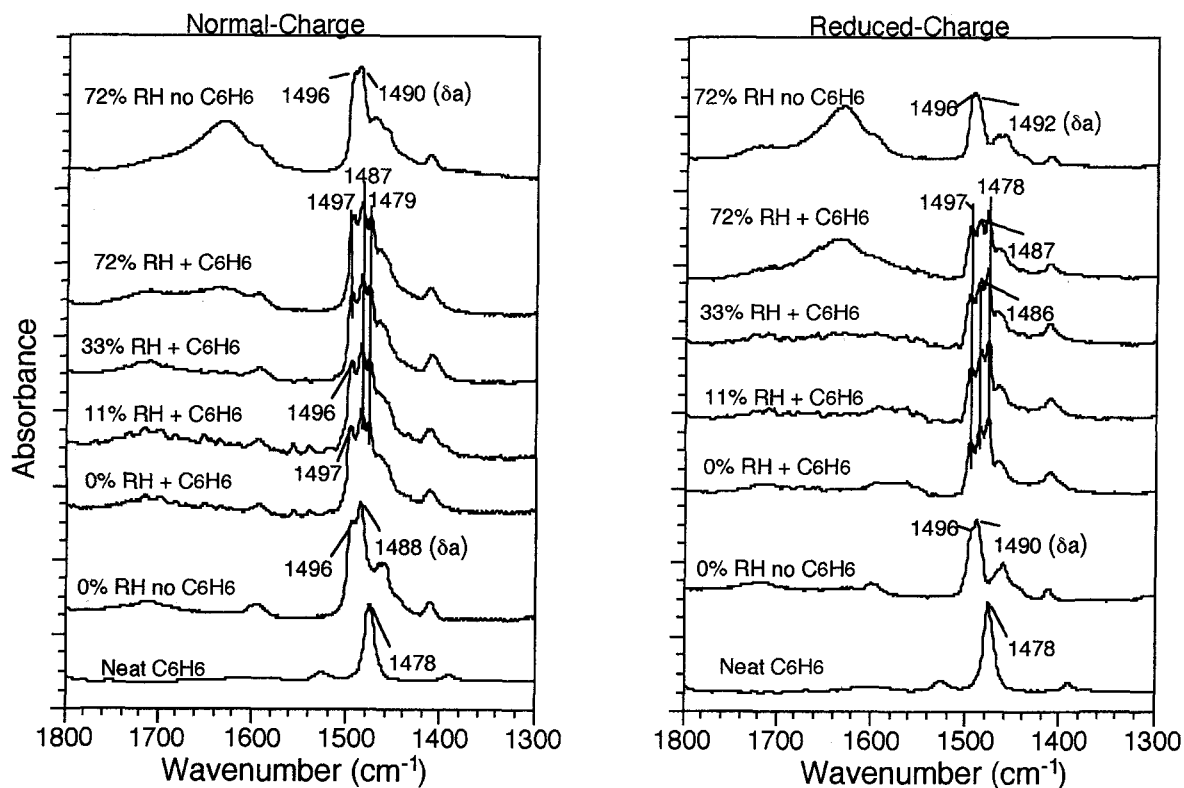


Figure 3. Infrared spectra of A) normal-charge and B) reduced-charge TMPA-montmorillonites with and without sorbed benzene (0 to 72% RH) and water (0 and 72% RH). Peak locations were estimated from peak maxima. Spectrum of neat benzene is shown at bottom.

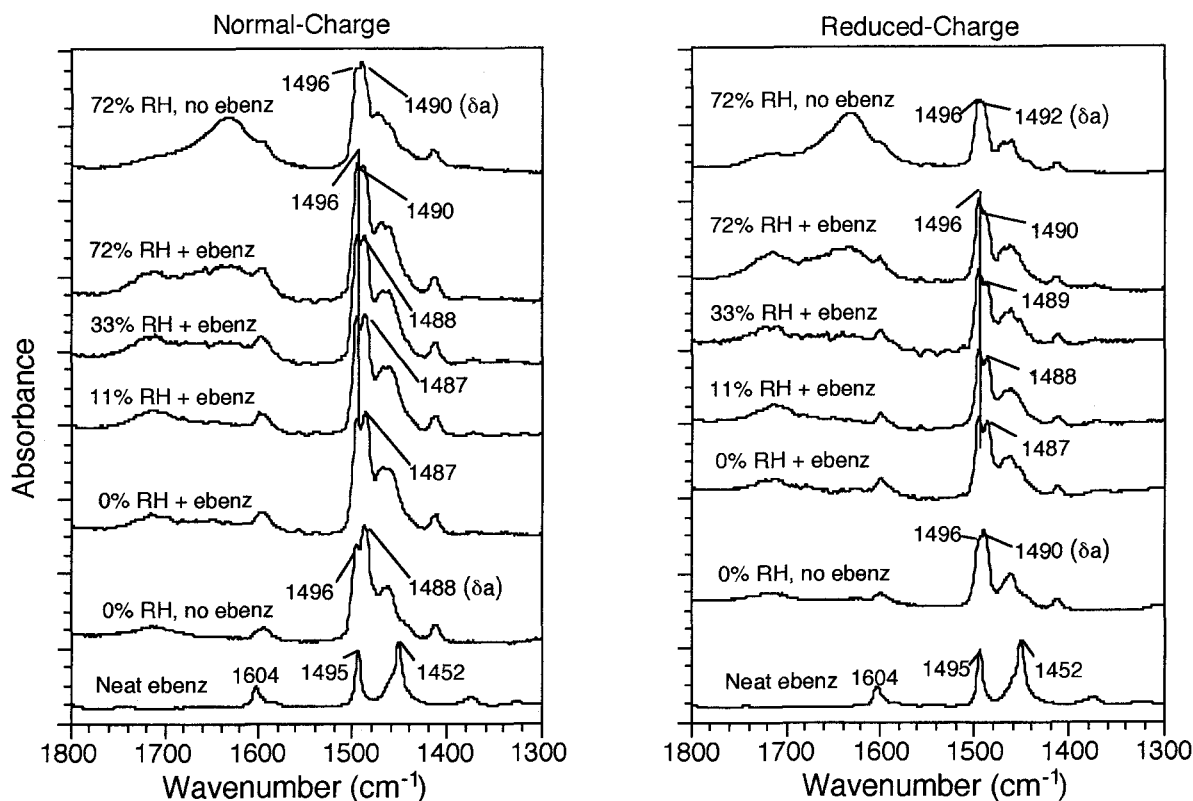


Figure 4. Infrared spectra of A) normal-charge and B) reduced-charge TPA-montmorillonites with and without sorbed ethylbenzene (0 to 72% RH) and water (0 and 72% RH). Peak positions were estimated from peak maxima. Spectrum of neat ethylbenzene is shown at bottom.

montmorillonites at 43% or 72% RH (Figures 1 and 2), the TMA δ_a peak shifted about 1 cm^{-1} to a higher wavenumber compared with its position on dry TMA-montmorillonite and no sorbate. Although the water-induced shifts are small, previous research indicates that the 1 cm^{-1} shift is part of a consistent trend of increasing δ_a wavenumber with increasing partial pressure of water (Stevens and Anderson 1996b). Because water sorption caused a shift to higher wavenumber and arene sorption caused a shift to lower wavenumber, the δ_a vibration of TMA is suited for studying changes in arene-TMA and water-TMA interactions when arenes and water both are present at increasing relative humidity. When both benzene- d_6 and water were adsorbed at 43% RH, the TMA δ_a vibration was at about 1482 cm^{-1} , the same frequency as when benzene- d_6 was sorbed in the absence of water (Figures 1A and 1B). The TMA δ_a frequency remained at 1482 cm^{-1} even at 100% RH, where the appearance of the clay films as well as the shape of water sorption isotherms (Stevens and Anderson 1996b) suggested that water had condensed on the clay. Furthermore, the same results were also obtained when the clay films were first equilibrated with water vapor only, then exposed to both benzene- d_6 and water vapor. Or first

equilibrated with benzene- d_6 , followed then with the benzene-water combination (data not shown). In contrast, when both ethylbenzene and water were sorbed at 72% RH (Figures 2A and 2B), the wavenumber of the TMA δ_a vibration was intermediate between its position when only ethylbenzene was sorbed and its position when only water was sorbed, but was closer to the position when water alone was adsorbed.

On both normal- and reduced-charge TPA-montmorillonites, water sorption in an arene-free atmosphere caused the TMA δ_a vibration to shift 2 cm^{-1} to higher wavenumber compared to the position on dry TPA-montmorillonite and no sorbate. This shift to higher wavenumber is opposite to the shifts caused by benzene and ethylbenzene sorption (Figures 3 and 4). When both benzene and water vapor were present at relative humidities up to 72%, the δ_a band of TPA on normal-charge montmorillonite stayed at the frequency characteristic of benzene sorption in the absence of water (Figure 3A). On reduced-charge montmorillonite, the TMA δ_a peak stayed at the frequency characteristic of noncompetitive benzene sorption at relative humidities up to 33%, then increased by 1 cm^{-1} as relative humidity increased to 72% (Figure 3B). When ethylbenzene and water competed for sorp-

tion sites on normal-charge TMPA-montmorillonite, the TMPA δ_a vibration shifted from the position characteristic of ethylbenzene sorption at 0% RH to the position characteristic of water sorption at 72% RH (Figure 4A). On reduced-charge TMPA-montmorillonite, the resulting position of the δ_a vibration at 72% RH was intermediate between the position when only ethylbenzene was sorbed and the position when only water was sorbed (Figure 4B).

HOH Deformation Band of Adsorbed Water

The HOH deformation band of adsorbed water ($\approx 1630\text{ cm}^{-1}$) provides spectroscopic evidence that benzene and ethylbenzene inhibit water adsorption on TMA- and TMPA-montmorillonites. On TMA-montmorillonite at 43% RH, the HOH deformation band was strongly absorbing when no benzene- d_6 was present, but barely rose above the baseline in the presence of benzene- d_6 (Figures 1A and 1B). In fact, the absorbance of this peak was greater in the absence of benzene- d_6 at 43% RH than in the presence of benzene- d_6 at 100% RH. Ethylbenzene sorption on TMA-montmorillonite at 72% RH also caused a great decrease in absorbance of the HOH deformation band of adsorbed water (Figures 2A and 2B). Similar results were obtained for TMPA-montmorillonites. The HOH bending vibration of water adsorbed on TMPA-montmorillonites at 72% RH was more intense in the absence of benzene or ethylbenzene than when either arene was present (Figures 3 and 4).

Other Vibrations

The C-H out-of-plane deformation vibration of sorbed benzene was near 690 cm^{-1} for normal- and reduced-charge TMA- and TMPA-montmorillonites and was unaffected by water sorption (data not shown). This shift to near 690 cm^{-1} is comparable to that previously reported for benzene physisorbed on Cu-montmorillonite (Doner and Mortland 1969; Mortland and Pinnavaia 1971). As is typical of physisorbed benzene, the positions of the ν_{19} bands of benzene (1478 cm^{-1}) and benzene- d_6 (1330 cm^{-1}) were not affected by water adsorption. In addition, the ν_{19} peak absorbance was the same at all relative humidities (Figure 1), which is evidence that water vapor had little effect on benzene adsorption at relative humidities up to 100%.

The CH_3/CH_2 and the C-H out-of-plane vibrations of sorbed ethylbenzene (≈ 1452 and 700 cm^{-1} respectively; Green 1962) were so weakly absorbing that their positions could not be determined with sufficient accuracy to determine whether water adsorption caused these peaks to shift. The ν_{19a} band of ethylbenzene (1495 cm^{-1} ; Green 1962), which occurs as a weak shoulder on the high-frequency side of the TMA and TMPA δ_a peaks, also was too weakly absorbing to determine its position accurately (Figures 2 and 4).

Benzene sorption caused the C-H out-of-plane deformation of TMPA to shift from 753 to 763 cm^{-1} on reduced-charge montmorillonite but caused no shift from 768 cm^{-1} on normal-charge montmorillonite (data not shown). Water sorption had the same effect as did benzene sorption, so the benzene-induced shift on reduced-charge montmorillonite is not evidence for π - π interactions between benzene and TMPA. Neither benzene, ethylbenzene, nor water caused shifts in the ν_{19a} vibration of TMPA (1496 cm^{-1}).

DISCUSSION

Sorption of benzene and ethylbenzene caused the methyl δ_a vibrations of both TMA and TMPA to shift to lower wavenumber on normal- and reduced-charge montmorillonites, whereas water sorption always caused the δ_a vibrations to shift to higher wavenumber when no aromatic sorbate was present. Thus, the positions of the methyl δ_a vibrations provide information about competition between water and arenes for adsorbed TMA and TMPA ions, as well as information about the effect of charge density and arene size on arene-alkylammonium interactions.

In general, benzene and ethylbenzene sorption caused larger shifts in the methyl δ_a vibrations of TMA and TMPA on reduced-charge than on normal-charge montmorillonites. The one exception was benzene- d_6 sorption on TMA-montmorillonite, for which the methyl δ_a peak shift was the same on reduced-charge as on normal-charge montmorillonite. If the magnitude of the bandshift is proportional to the fraction of methyl groups that interact with benzene and ethylbenzene, the generally greater shifts for reduced-charge TMA- and TMPA-montmorillonites suggest that benzene and ethylbenzene interact with a larger proportion of TMA and TMPA ions on reduced-charge than normal-charge montmorillonite. On reduced-charge montmorillonite, the space between adjacent alkylammonium ions likely is sufficient to allow benzene and ethylbenzene to diffuse between the cations and penetrate most or all of the interlayer region, and thus to interact with most or all of the interlayer TMA and TMPA ions. On normal-charge montmorillonite, where the space between adsorbed cations is only about half that on reduced-charge montmorillonite (Stevens and Anderson 1996a), adsorbed cations may be so close together that benzene and ethylbenzene can't penetrate all of the interlayer region, with the exception of benzene- d_6 on TMA-montmorillonite. For benzene- d_6 sorption on TMA-montmorillonite, the identical shifts for normal-charge and reduced-charge montmorillonite indicate that benzene can interact with about the same proportion of TMA ions on normal-charge as on reduced-charge montmorillonite. This result may be due to the relatively small sizes of benzene compared to ethylbenzene and TMA compared to TMPA.

On TMA-montmorillonite, benzene- d_6 sorption

caused a larger shift in the methyl δ_a vibration of adsorbed TMA than did ethylbenzene sorption. If each benzene- d_6 molecule perturbs the TMA δ_a vibration by the same amount as does each ethylbenzene molecule, the greater δ_a bandshift in the presence of benzene d_6 would suggest that more TMA ions interact with benzene- d_6 than with ethylbenzene. Benzene, which is smaller than ethylbenzene, probably can interact with TMA ions that reside in interlayer regions that are inaccessible to ethylbenzene; ethylbenzene may be too large to diffuse into some interlayer regions, particularly on normal-charge TMA-montmorillonite, where the space between cations is smaller.

The effect of arene size on cation-arene interactions was less important for TMPA-montmorillonite than for TMA-montmorillonite. On normal-charge TMPA-montmorillonite, benzene caused essentially the same shift in the TMPA δ_a vibration as did ethylbenzene. On reduced-charge montmorillonite, benzene caused only a 1 cm^{-1} larger shift than did ethylbenzene, which may not be a significant difference. These results are consistent with the observation (Jaynes and Boyd 1990, 1991) that substituent chain length had only a small effect on alkylbenzene sorption by TMPA-montmorillonites whose adsorbed TMPA concentrations were similar to the clays used in the present study. On our reduced-charge TMPA-montmorillonite, the average space between adjacent TMPA ions, 52 \AA^2 (Stevens and Anderson 1996a) is sufficient to allow diffusion of either benzene or ethylbenzene, so both arenes cause about the same shift in the methyl δ_a vibration. On normal-charge TMPA-montmorillonite, however, the 25 \AA^2 average space between cations is just equal to the edge area of benzene. Given that layer charge is not distributed uniformly throughout the crystal structure of smectites, there likely are some TMPA ions that are separated by more than 25 \AA^2 and some separated by less than 25 \AA^2 . Those TMPA ions that are separated by less than 25 \AA^2 would be equally inaccessible to both benzene and ethylbenzene, while both of these arenes would be able to interact with TMPA ions that are separated by sufficiently large distances. As a result, on normal-charge TMPA-montmorillonite, benzene causes the same small shift in the TMPA δ_a peak as does ethylbenzene.

To study arene-water competitive adsorption at high relative humidity, the clay films were equilibrated overnight with both water vapor ($P/P_0 = 0.72$ or 1.0) and benzene, benzene- d_6 or ethylbenzene ($P/P_0 = 1.0$), then were transferred to an infrared cell that contained water but no arene, about 75 min before spectra were acquired. During the overnight reaction time, the activity (vapor pressure) of benzene was about five times greater than that of water, which in turn was about twice that of ethylbenzene. In the infrared cell, however, the activity of water was greater than the activity of either arene. Under these conditions, the TMA and

TMPA δ_a peak positions showed that the adsorbed cations interacted with benzene rather than with water, but interacted more with water than with ethylbenzene. The predominance of benzene-cation interactions over water-cation interactions and of water-cation interactions over ethylbenzene-cation interactions, appears to depend upon sorbate vapor-phase activities during the overnight reaction time than during the 75-min reaction in the infrared cell. Possibly because the clay films may not have reached equilibrium with the arene-free atmosphere in the infrared cell. Alternately, the predominance of benzene-cation interactions over water-cation interactions may mean that TMA and TMPA have greater affinity for benzene than for water. Additional experiments would be required to test either of these explanations.

The predominance of water-cation interactions over ethylbenzene-cation interactions during competitive ethylbenzene/water sorption at 72% RH indicates that ethylbenzene has little effect on water-cation interactions. Nevertheless, ethylbenzene greatly inhibited total water sorption on TMA- and TMPA-montmorillonite, as shown by the much lower absorbance of the water HOH deformation band in the presence of ethylbenzene. Consequently, ethylbenzene must inhibit water sorption on the siloxane surface. Benzene also must inhibit water sorption on the siloxane surface, because benzene and benzene- d_6 reduced the absorbance of the HOH deformation peak as much as did ethylbenzene. The C-H out-of-plane vibration of sorbed benzene, which was at nearly the same wavenumber as previously reported for physisorbed benzene on the siloxane surfaces of Cu- and other metal-cation-saturated montmorillonites (Doner and Mortland 1969; Mortland and Pinnavaia 1971), is also consistent with the siloxane surface being the most important sorption site for benzene, both in the presence and absence of water.

In summary, our infrared data shows that in the absence of water, benzene and ethylbenzene interact with adsorbed TMA and TMPA ions, as well as adsorb on the siloxane surface. The greater arene-induced shifts in the methyl δ_a vibrations of TMA and TMPA on reduced-charge than on normal-charge montmorillonite indicate that some interlayer regions of normal-charge montmorillonite are inaccessible to arenes. In addition, some interlayer regions of TMA-montmorillonite, but not TMPA-montmorillonite, apparently are more accessible to benzene than to ethylbenzene. When water and arene vapors both are present, water sorption inhibits arene-cation interactions but has little or no effect on arene sorption by siloxane surfaces. In contrast, both benzene and ethylbenzene greatly inhibit water sorption on the siloxane surface even when the activity of water is many times greater than the activity of benzene or ethylbenzene in the infrared cell. These results suggest that in an aqueous solution, where the activity of water would be more than 1000

times greater than arene activity, water would inhibit arene sorption primarily by hydrating the adsorbed cations; arene sorption would occur primarily on the siloxane surface, as proposed previously by Jaynes and Boyd (1991).

ACKNOWLEDGMENTS

This research was supported in part by a CMS student research grant to JJS, in part by a research initiation grant from Dow Chemical to SJA and SAB, and in part by the Michigan Agricultural Experiment Station.

REFERENCES

- Boyd SA, Jaynes WF, Ross BS. 1991. Immobilization of organic contaminants by organo-clays: Application to soil restoration and hazardous waste containment. In: Baker RS, editor. *Org Substances and Sediments in Water*, vol. 1. Boca Raton, FL: CRC Press. 181–372.
- Brindley GW, Ertem G. 1971. Preparation and solvation properties of some variable charge montmorillonites. *Clays & Clay Miner* 19:399–404.
- Doner HE, Mortland MM. 1969. Benzene complexes with copper(II) montmorillonite. *Science* 166:1406–1407.
- Duinker JC, Mills IM. 1968. Normal coordinates for the planar vibrations of benzene. *Spectrochim Acta* 24A:417–435.
- Green JHS. 1962. Vibrational spectra of benzene derivatives—III. Anisole, ethylbenzene, phenetole methyl phenyl sulphide and ethyl phenyl sulphide. *Spectrochim Acta* 18: 39–50.
- Greene-Kelly R. 1953. The identification of montmorillonoids in clays. *J Soil Sci* 4:233–237.
- Jaynes WF, Bigham JM. 1987. Charge reduction, octahedral charge, and lithium retention in heated, Li-saturated smectites. *Clays & Clay Miner* 35:440–448.
- Jaynes WF, Boyd SA. 1990. Trimethylphenylammonium-smectite as an effective adsorbent of water soluble aromatic hydrocarbons. *J Air Waste Management Assoc* 40:1649–1653.
- Jaynes WF, Boyd SA. 1991. Hydrophobicity of siloxane surfaces in smectites as revealed by aromatic hydrocarbon adsorption from water. *Clays & Clay Miner* 39:428–436.
- Lee JF, Mortland MM, Chiou CT, Kile DE, Boyd SA. 1990. Adsorption of benzene, toluene, and xylene by two tetramethylammonium-smectites having different charge densities. *Clays & Clay Miner* 38:113–120.
- Mortland MM, Pinnavaia TJ. 1971. Formation of copper(II) arene complexes on the interlamellar surfaces of montmorillonite. *Nature Phys Sci* 229:75–77.
- Stevens JJ, Anderson SJ. 1996b. Orientation of the phenyl group of trimethylphenylammonium on normal- and reduced-charge Wyoming montmorillonite. *Clays & Clay Miner* 44:132–141.
- Stevens JJ, Anderson SJ. 1996c. An FTIR study of water sorption on tetramethylammonium- and trimethylphenylammonium-saturated normal- and reduced-charge Wyoming montmorillonite. *Clays & Clay Miner* 44:142–150.
- Varsányi G. 1969. *Vibrational Spectra of Benzene Derivatives*. New York and London: Academic Press. 430 pp.
- Weast RC, editor. 1986. *CRC Handbook of Chemistry and Physics* 67th ed. Boca Raton, Florida: CRC Press, Inc. D189–D212.

(Received 22 September 1994; accepted 23 May 1995; Ms. 2576)